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Grass Waste: A Highly Biosorbent for the Removal of Malachite Green Dye From Aqueous Solution

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ABSTRACT

Grass waste (GW), a low-cost agricultural waste, is a more effective adsorbent to remove malachite green MG dye. Treatments physical or chemical of GW by soaking in solution H_2O_2 (10%) for 4 hours at 25 °C. The removal of MG from bio-sorption GW was studied at several weights of GW (0.01–0.1 g), equilibrium time (2–120 min), initial concentration (10–100 mg/L), and pH solution (2–10). The effect of the factors on the adsorption efficiency was studied using the batch process. Increasing MG dye concentration, the adsorption efficiency of GW increased, but the removal percentage decreased from 10.599 mg/g to 110.99 mg/g to 94.11% to 83.08%. The data evidently displayed a removal percentage of MG of about 89.89% at a weight of GW of 0.08 g/100 mL. The adsorbent was characterized via SEM and TEM. Desorption of MG dye studies was performed with hydrochloric acid, sodium hydroxide, phosphoric acid, acidic acid, and H_2O. A high removal percentage of 89.088% in acid medium 0.1 N hydrochloric acid. With the addition of HCl, the solution pH decreases, and hence, at a pH of 3, the GW surface becomes large and protonated, and the attachment among the molecules of dye and GW becomes weakened. The data revealed that bio-sorption GW adsorbent is potentially a very low-cost and eco-friendly adsorbent for the removal of MG dye.

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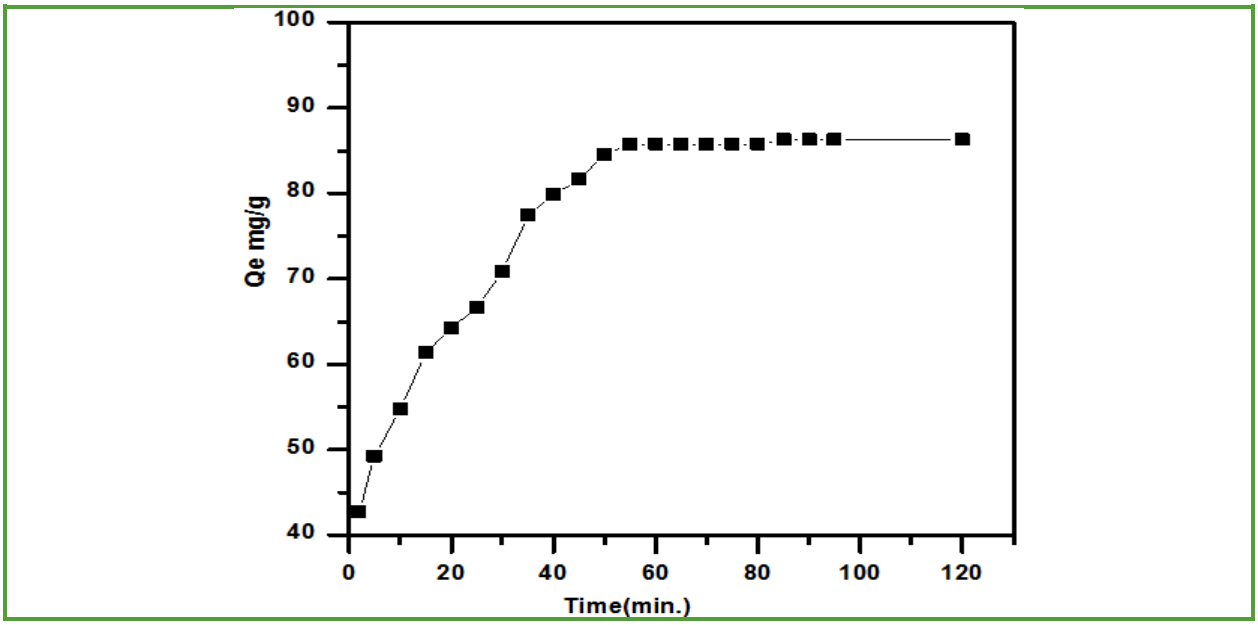
Graphical Abstract



Introduction

Treatment of liquid waste resulting from textile and related industries is a global environmental issue. Effluents derived from textile waste and dyes can cause serious environmental problems affecting neighboring receiving water bodies due to the presence of toxic dyes, chlorine residues, and dark-colored dyes [1, 2]. The process of removing textile dyes from wastewater using adsorption on commercial activated carbon is very effective, but has a high cost and has therefore been replaced by cheap, readily available, and low-cost adsorbents. Biosorption is recognized as an economically efficient approach for removing dyes. Several low-cost agricultural wastes such as rice husk, peanut shell, rejected tea, and fruit peels such as, orange shell, banana husk, jackfruit husk, grapefruit shell, custard apple shell, and pomegranate peel are utilized as sorbents to removal of dyes [3-6]. The stability and adsorption capacity of raw bio-mass can be further improved *via* chemical modification and activation. Accordingly, several agricultural wastes have been chemically modified and proven to be better sorbents for the removal of dyes. Researchers have increasingly explored low-cost alternative adsorbents to replace expensive commercially available activated carbon. This alternative includes: bio sorbents, agricultural waste, natural materials, and by-products of industrial experiments [7-15]. Table 1 presents some of the adsorbents used to remove textile dyes from aqueous solutions. In this study, weed waste was used as a highly effective, new, unconventional, and low-cost adsorbent to remove Malachite green (MG) from the aqueous solution. To make better use of this widely available agricultural waste, the weed waste was activated with hydrogen peroxide and converted into activated carbon with highly effective in removing dyes. Therefore, the primary purpose of the study work was to evaluate the potential of high grass waste adsorption of textile dyes from aqueous solution.

Table 1. Recent research on adsorption of dyes via several adsorbents

Adsorbent	dyes	Qe (mg/g)	Reference
Sunflower seed hull	Methyl violet	92.29	[4]
Biomass fly ash (FA-BM)	Reactive black 5	4.38	[16]
Broad bean peels	Methylene blue	192.7	[9]
Solis waste of soda ash plant	Reactive red 231	667	[17]
Apricot stone source waste	Mb	156	[18]
Coconut husk	MB	144.5	[19]
Coconut husk	crystal violet	122.6	[19]
Untreated desert plant	MB	23	[20]
Pyrolized desert plant	MB	53	[21]
Chitosan bead	MG	93.55	[10]
Soy meal hull	Direct red 80	178.57	[22]
Soy meal hull	Acid blue 92	114.943	[22]
Luffa cylindrical fibers	Methylene blue	47	[23]
Grass waste	Malachite green	89.99	In this study

Experimental

Material and Methods

Malachite green (MG) dye and stander MG dye solution purchased from Sigma–Aldrich was utilized as model dye. A stander solution of dye 1000 mg/L was prepared via dissolving 1 g of dye in 1000 mL of DW. The all solutions were prepared via diluting the stock solution with distilled water (DW) to give several concentrations of solutions. Solution pH was adjusted with 0.1 N NaOH or HCl.

Preparation of grass waste (GW)

The grass waste (GW) was collected from the home garden in Hilla, Iraq. The GW was washed, dried, grinded, and sieved to the desired mesh size (50-100 nm). Without treatments, physical or chemical, prior to adsorption experiments. GW was soaked in a solution H_2O_2 at 4% s for 4 h at 25 °C to remove impurities that were soluble. The clean GW was repeatedly washed utilizing DW till a neutral pH of 7 was attained, and then dried at 66 °C for 24 h. The sample was stored in an airtight container for further utilization.

Adsorption isotherm

The influence of adsorbent dosages was studied via addition several quantities of GW of 0.01-0.1 g/100 mL solution. In the adsorption equilibrium investigation, 0.08 g of GW was added to a 100-mL adsorbate containing MG dye concentrations ranging from 10 to 100 mg/L at 25 °C and a solution pH of 6.8. The pH solution adjustments were carried out via addition NaOH or HCl 0.1 N. This experiment was conducted in batch adsorption for 60 min. After the adsorption constant was reached, the MG dye concentration was estimated via UV-Vis spectrophotometer. The adsorption efficiency (Qe mg/g) and percentage removal R% are described in Equations (1) and (2).

$$R\% = \frac{Co - Ce}{Co} \times 100 \quad (1)$$

$$Qe = \frac{(Co - Ce)V}{w} \quad (2)$$

Where, R% is the percentage of removal, Qe is adsorption capacity, C_0 is the initial concentration, C_e is the equilibrium concentration, V is the volume of solution under study, and w is the mass of the adsorbent surface.

Result and Discussion

FE-SEM (Field Emission Scanning Electron Microscopy)

The surface appearance of GW is displayed in Figure 1a, b. The SEM in Figure 1a micrograph of GW before the adsorption process shows irregular shapes containing cavities and gaps. In addition, the GW shape differs in their dimensions, as dimensions (500 nm), where the surface has irregular shapes It is probable to find very great particles as well as small particles randomly scattered on the surface. Also, in Figure 1b after adsorption with 500 nm magnification, the SEM image show that the surface has the form of thin sheets grouped together. This indicates an increase in the surface area and confirms the success of the adsorption process [13, 24, 25].

To limit the size, shape, and particle distribution of GW, TEM analysis was performed. As appear in Figure 1c, dark-colored semispherical aggregates enclosed within a matrix-like structure were found, which can be attributed to the method of washing with H_2O_2. The method of washing rises porosity of the surface [26].

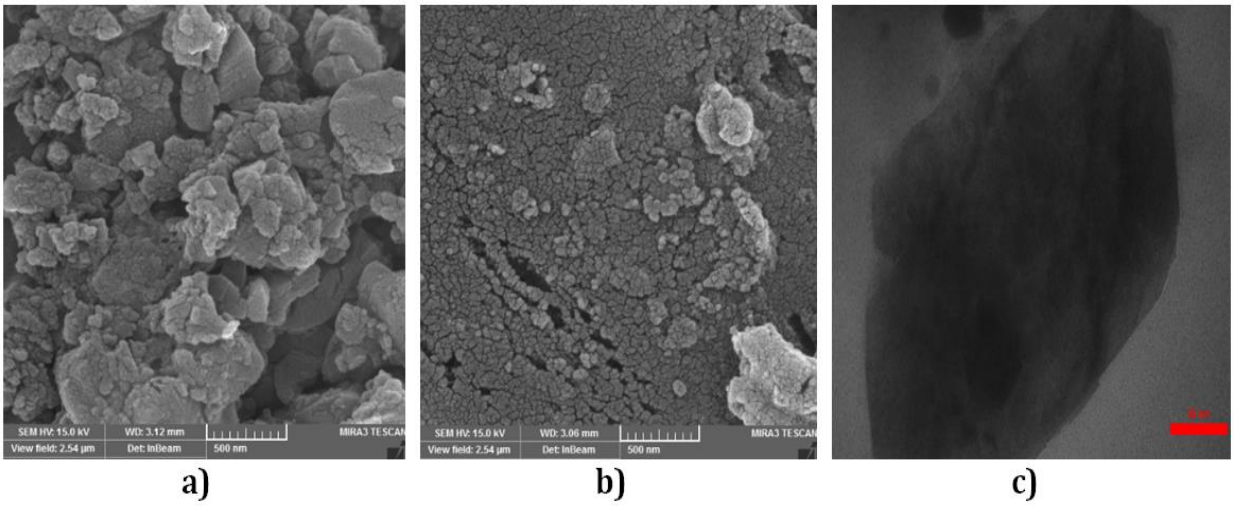


Figure 1. FE-SEM of GW surface a) before, b) after adsorption, and c) TEM of GW

Effect of contact time

Removal of MG dye by Bio-sorption GW was studied as an equilibrium time by utilizing weight of GW (0.08 g/100 mL), concentration of MG (50 mg/L), and pH solution 6.8, as depicted in Figure 2. Bio-sorption equilibrium can be established via studying the equilibrium time parameter, which is significant in the bio-sorption method. Figure 2 illustrates the effect of this parameter on MG onto GW. Bio-sorption of MG was rapidly in the first 2-10 min, the rate of GW adsorption gradually decreased, reaching a plateau after 60 minutes, with the optimal adsorption capacity observed at 89.54 mg/g. The contact time of 60 min was intended in the following experiments when there was no important rise in acceptance after this time. For explanation, at the initial steps of bio-sorption, the uptake rate MG is very important as more existing bio-sorption sites molecules of MG, and then these sites are commonly full up, and bio-sorption becomes slow because of MG accumulation at the GW surface. Because of this accumulation, the diffusion inside of molecules MG into the GW pores became difficult [27-29].

Effect of pH

The pH is important for MG dye solution as it is considered an operating factor that controls the removal of dye on the prepared surfaces because it depends on the surface charge and the dye molecules are also affected *via* the solution pH, as demonstrated in Figure 3. It can be shown that the removal percentage and adsorption efficiency increase with rising pH of the solution dye, reaching a maximum value at pH 6.8 (89.08%) (94.545 mg/g), so the pH value in the dye solution, pH 6.8, was adopted in all experiments. The reason for the increase in the basic medium is due to the increase in negatively charged sites on the GW, which leads to a favorable electrostatic attraction among the GW and the cationic dye. The decrease percentage removal and adsorption efficiency at low pH is further due to the protons present on the GW surface, which causes electrostatic repulsion between the surface and the dye [18].

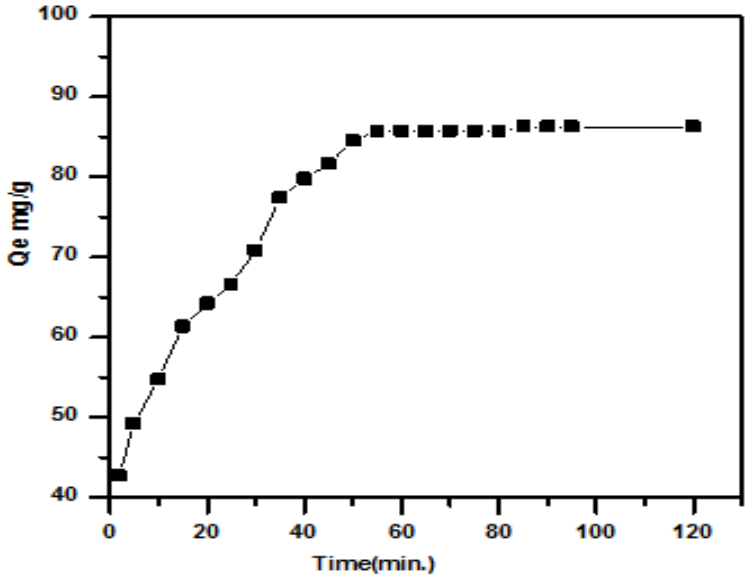


Figure 2. Effect of equilibrium time onto removal % of MG dye by GW

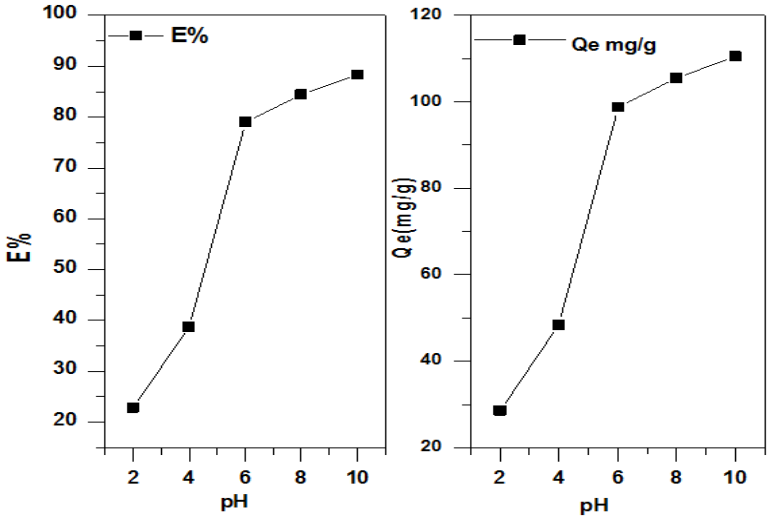


Figure 3. Effect of pH solution onto adsorption capacity MG dye onto GW

Effect of adsorbent dosage

GW weight is an important parameter in estimation of extent of elimination of MG dye, dependent upon adsorption efficiency of adsorbent and optimum conditions. The removal % of MG via GW was studied as a function of changing weight of GW (0.01-0.1 g/100 mL) at concentration MG dye (50 mg /L) for 60 min. Figure 4 displays a quick phase of mass of GW increase in removal MG dye up to 0.08 g/100 mL weight of GW and that was followed a sluggish phase of E% of MG dye among of doses of adsorbent 0.08 and 0.1 g/100 mL [4, 30-32]. The data evidently displayed removal percentage of MG about 89.89 % at weight of GW of 0.08 g/100 mL. The bi-phasic pattern of dose dependent elimination MG dye could be interpreted in terms of primary dose dependent quick removal MG due to the increased accessibility of MG binding sites and greater surface area, whereas sluggish phase of MG elimination may be the overleaping and shadowing influence of extra GW on binding ligands and thereby, data in to decrease availability of the molecules of dye to the active site [33-35].

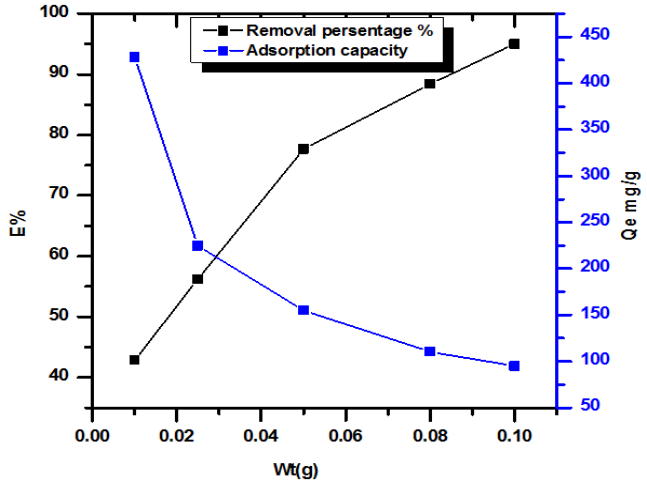


Figure 4. Effect of GW weight onto removal percentage, and adsorption capacity MG dye

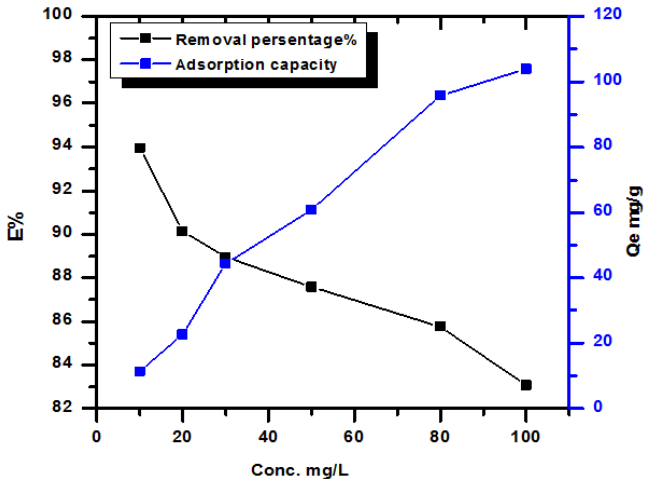


Figure 5. Effect of several concentrations onto removal percentage, and adsorption capacity by GW

Table 2. Removal percentage % of MG dye in several desorbing agents

Desorbing agents	Removal percentage (%)
Fresh	89.895
HCl	86.089
NaOH	73.78
H_2O	70.98
CH_3COOH	62.89
H_3PO_4	55.98

Effect of MG dye concentration

The removal percentage of MG dye via GW is dependent on the primary MG dye concentration from aqueous medium. The influence of primary MG dye concentration on the sorption capacity of GW depend on the accessibility of MG molecules and active sites present onto GW. The influence of several MG dye concentration (10–100 mg/L) on the adsorption capacity of GW was studied, utilizing mass of GW (0.08 g/100 mL) and pH 6.8 at 25 °C [1, 2, 33]. Figure 5 illustrates the primary MG dye concentration dependent quick rise in the rate of elimination percentage % MG dye up to 60 min. The rate constant of MG adsorption at adsorption capacity (Qe mg/L) was found to rise from 9.987 mg/g to 115.87 mg /g with increase of MG dye concentration from 10 to 100 mg/L. Increasing MG dye concentration, the adsorption efficiency of GW increased, but removal percentage % decreased from (94.98-83.38%). At higher MG dye concentrations [9, 23, 36].

Adsorption-desorption of MG

The use several mineral (HCl 0.1 N, H_3PO_4 0.1N, NaOH 0.1 N and H_2O) to be large removal of dye from MG -loaded GW as compared with other agents, as indicated in Table 2. A great removal % of (83.089%) in acid medium 0.1N hydrochloric acid [37]. HCl addition initially decreases solution pH and hence, at little solution pH 3, the GW surface become large protonated and the attachment among molecules of dye and GW become weakened [38].

Conclusion

Bio-sorption GW, an available agricultural waste material, can be utilized as an adsorbent to adsorb positive MG dye from aqueous medium without any chemical treatment. The results are that dye removal depends on the dye removal depends on the amount of GW used in the adsorption process, under the experimental conditions of pH and equilibrium time. The best adsorption capacity (Qe mg/g) of GW was 89.04 mg/g after 60 min of equilibrium time at pH 6.8 at 25 °C. Likewise, it was concluded that GW, was used without any chemical treatment, GW is an inexpensive, environmentally friendly absorbent material characterized by its high dye removal capabilities, which can be has been demonstrated to exhibit superior performance compared to expensive commercial absorbent materials available in the market through recycling via the surface more than once to remove contaminants (dyes) from their aqueous solution.

Disclosure Statement

No potential conflict of interest was reported by the authors.

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Authors' Contributions

All authors contributed to data analysis, drafting, and revising of the article and agreed to be responsible for all the aspects of this work.

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